

Pressure-Induced Cation Migration and Volume Expansion in Defect Pyrochlore Oxides

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Beamline(s): X7A

Introduction: Microporous materials, such as zeolites [1,2], undergo pressure-induced volume expansion (PIE) under increasing pressure. Previously, NH_4NbWO_6 (a defect pyrochlore) was shown to undergo pressure-induced expansion in hydrostatic media containing water [3]. The PIE observed in NH_4NbWO_6 was attributed to forceful insertion of water molecules into the pyrochlore structure. Due to the experimental setup used (energy dispersive x-ray diffraction), details of PIE in NH_4NbWO_6 could not be determined. By examining a series of different ANbWO_6 pyrochlores using monochromatic synchrotron x-ray powder diffraction, the details and mechanism of PIE in these compounds was explored.

Methods and Materials: The structural and compositional evolution of four members of the ANbWO_6 ($A = \text{NH}_4^+$, H^+ , Rb^+ , K^+) defect pyrochlore family have been studied as a function of pressure up to 7 GPa, using a diamond anvil cell and monochromatic synchrotron X-ray powder diffraction. Pressures exerted by the diamond anvil cell on the sample were measured using laser fluorescence spectroscopy.

Results: In response to increasing hydrostatic pressure, NH_4NbWO_6 and RbNbWO_6 both initially contract, but then undergo a fairly abrupt increase in their unit cell volume above a characteristic threshold pressure. In agreement with previous studies [3], NH_4NbWO_6 exhibits a 5.8% increase in the cubic unit cell edge once the pressure exceeds ~ 3.4 GPa. The increase in volume exhibited by RbNbWO_6 (figure 1) first observed in this experiment is larger ($\sim 7.5\%$) than seen in the ammonium compound but is less abrupt, beginning near 3.0 GPa. Rietveld refinements reveal that the reversible expansion is driven by insertion of water into the structural channels, which interpenetrate the NbWO_6 octahedral corner sharing framework. The insertion of extra water is accompanied by displacement of the NH_4^+ or Rb^+ ions to a smaller site in the channel structure, which triggers the pressure-induced expansion of the pyrochlore framework. Similar behavior is not observed for $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ or $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$, both of which contract in response to increasing pressure. For these smaller monovalent cations, pressure-induced volume expansion does not occur because the hydrated state, and subsequent cation shift, are already stable at ambient conditions.

Acknowledgments: Research carried out in part at the NSLS at BNL is supported by the U.S. DoE, Division of Materials Sciences and Division of Chemical Sciences (DE-Ac02-98CH10886 for the X7A beamline). We acknowledge the Geophysical Lab of the Carnegie Institute for allowing us the use of the ruby laser system associated with the beamline X17C.

References:

- [1]. I. A. Belitsky, B. A. Fursenko, S. P. Gabuda, O. V. Kholdeev, Yu. V. Seryotkin, "Structural Transformations in Natrolite and Edingtonite," *Physics and Chemistry of Minerals*, **18**, 497-505 (1992).
- [2]. Y. Lee, T. Vogt, J. A. Hriljac, J. B. Parise, G. Artioli, "Pressure-Induced Volume Expansion of Zeolites in the Natrolite Family," *Journal of the American Chemical Society*, **124**, 5466-5475 (2002).
- [3]. C. A. Perottoni, J. A. H. da Jornada, "Pressure Induced Water Expansion in the Defect Pyrochlore NH_4NbWO_6 ," *Physical Review Letters*, **78**, 2991-2994 (1997).

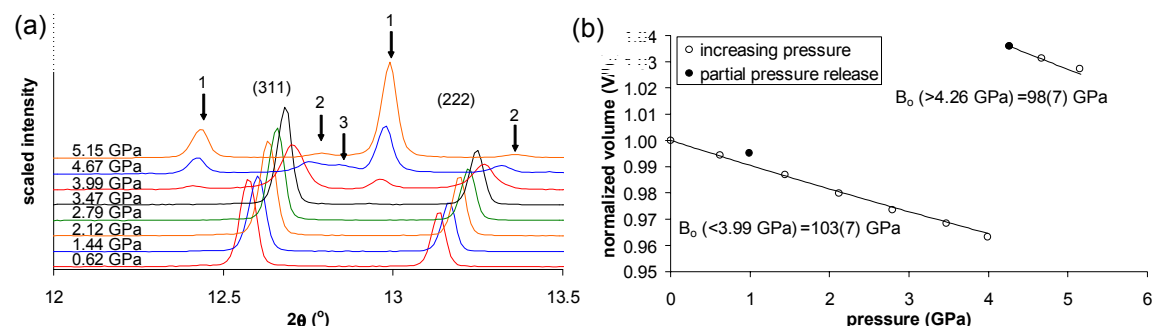


Figure 1. (a) Partial x-ray diffraction patterns for RbNbWO_6 (cubic; space group $Fd3m$). Note the formation of at least two phases at pressures greater than 3.99 GPa. Reflections marked with "1" correspond to the hydrated phase, and those marked with "2" are related to the original compound. The peak marked "3" corresponds to the strongest reflection of a third cubic phase (origin and composition unknown). (b) Pressure dependence of the unit cell volume of RbNbWO_6 . At pressures ≥ 3.47 GPa, V/V_0 is given for the majority phase only. Bulk moduli (B_0) were calculated by fitting a second order Birch-Murnaghan equation of state (plotted in the figure) to the normalized volumes, where $B' = 4$.